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Time-dependent density functional theory for periodic systems

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Summary

In this thesis the time-dependent version of density functional theory is described, which has been developed for crystalline non-metallic systems with periodicity in one to three dimensions. The application of this theory to the calculation of the optical response properties of a wide range of materials proved to be very successful.

The description of an interacting many-particle systems is, in general, very complicated and approximations need to be made. Many methods in quantum chemistry try to describe the motion of the electrons in such systems by the electronic wavefunction, the solution of the time-dependent Schrödinger equation. The computational effort involved in these methods, for the evaluation of the electronic wavefunction, is very high, contrary to density functional theory (DFT), in which the computational costs are much lower. In DFT, not the electronic wavefunction is evaluated for a full description of the interacting many-particle system, but it is sufficient to look at the electron density. The fundamental theorems for this theory were first formulated in the early 1960s by Hohenberg and Kohn, and, for practical use, incorporated, shortly after, in a one-electron self-consistent field calculation scheme by Kohn and Sham. In this Kohn-Sham approach to density functional theory, the interacting many-particle system is modelled in terms of an effective non-interacting particle system, called the Kohn-Sham system. The effective external field, to which this Kohn-Sham system is subjected, incorporates the true external field and, in an effective way, the interparticle interactions. The modelling of the effective potential, which is called the Kohn-Sham potential, is done in such a way that the electron density of the non-interacting Kohn-Sham system exactly reproduces the electron density of the true interacting many-particle system. The Kohn-Sham potential is thus a functional of the electron density, however, this density can only be obtained if this Kohn-Sham potential is known. Both the electron density and the Kohn-Sham potential can be obtained in a self-consistent field scheme in which self-consistency is achieved for the electron density. The electron density and the Kohn-Sham potential are hereby updated in an iterative way. In the time-dependent extension of DFT, the external potential varies in time, and consequently also the electron density and effective potential become time-dependent.

After a brief and short introduction of the concepts behind time-dependent density functional theory in Chapter 2, we discuss in Chapter 3 the polarization of a dielectric medium. We show that, when polarization in such a dielectric medium is introduced as the dynamic response of the system to an externally applied electric field, the definition of polarization in terms of the induced current flowing through the system provides an elegant way

to avoid the problems as faced in the description of polarization in terms of the electron density. Such definitions of polarization are always ill-defined, because they depend on the particular choice of partitioning the system into separate elements. When the concept of polarization in a dielectricum is defined in terms of the induced current flowing through the system, these problems are circumvented. The definition in terms of the induced current is also more attractive because in this way it is not necessary to consider the surface of the system explicitly. The charge that piles up at the surface of the system is after all directly related to the induced current flowing through the interior of the system.

Our approach to time-dependent density functional theory (TDDFT) for the description of the dielectric properties of crystalline solids is described in Chapter 4. The solids, modelled as ideal lattice periodic systems, are treated in the presence of time-dependent electromagnetic fields. This description requires the combination of uniform electric fields with lattice periodic effective potentials. A perturbative approach to the time-dependent self-consistent field scheme is used, involving both the density and the current density in a real space description, in contrast with many other approaches that use a description in reciprocal space. Advantage is the high spatial resolution achieved, and the flexibility to use various potentially very complicated functionals of the density and the current density. The electric susceptibility can then be obtained if the macroscopic polarization is derived from the induced current density. The elegant and efficient iterative calculation scheme, as implemented in the state of the art full-potential periodic version of the Amsterdam Density Functional (ADF-BAND) code, is described. Some features of the implementation are, the use of a linear combination of atomic orbitals as a basis and linear response theory in which Coulomb interactions and exchange-correlation effects are included. Further, the explicit evaluation of the Kohn-Sham response kernels is avoided by treating these kernels analytically and the Coulomb integrals are evaluated by the use of auxiliary fitfunctions, and also a screening technique is used to evaluate the lattice sums.

The success of our TDDFT approach, as introduced in Chapter 4, becomes clear when looking at the results presented in Chapter 5. There the dielectric constants and functions for a variety of elemental and binary crystals are presented. Already within the adiabatic local density approximation for the exchange-correlation functional, we get good agreement with experiment. The accuracy of the dielectric constants is about 5%, and the spectral features in the dielectric functions are well reproduced, but appear at energies that are rigidly shifted towards lower energies.

The only exceptions, however, were found for InSb and HgSe in the zincblende structure. Their static dielectric constants were underestimated by about 40% when compared with experiment. A further analysis, presented in Chapter 6, showed that these deviations are caused by relativistic effects. We demonstrated that our TDDFT approach can also be applied successfully for the description of these zincblende materials when relativistic effects are included in TDDFT within the so-called zeroth order regular approximation (ZORA). Thereby drastic effects on the dielectric properties for these materials were observed. The materials InSb and HgSe turn into semimetals due to relativistic effects, because, within the local density approximation, their bandstructures were inverted. Now, with the inclusion of scalar relativistic effects, the same order of accuracy of about 5% relative to

experiment was achieved for the static dielectric constants. The dielectric functions were greatly improved, and are now also found in good agreement with experiment.

In a first attempt to go beyond the adiabatic local density approximation we investigated in Chapter 7 a polarization functional. The effects on the absorption spectra of various semiconductors are presented. This polarization functional, as derived by Vignale and Kohn, includes the exchange-correlation contributions in the effective macroscopic electric field. For all the semiconductors for which we tested this polarization functional, the optical absorption spectra showed a better agreement with experiment than when the spectra were calculated within the adiabatic local density approximation.

In Chapter 8 we demonstrate that TDDFT describes the excitonic effects correctly in some solids. Perturbing a solid by an electromagnetic field can cause the formation of bound electron-hole pairs which are called excitons. Such an exciton is usually understood as an additional two-particle interaction in the effective one-particle picture, namely as the Coulombic interaction between an excited electron in the conduction band, and the hole which this electron leaves behind in the valence band. For the investigated systems: CaF_2 , SiO_2 and GaN , it is shown that TDDFT, in the adiabatic local density approximation, is already capable to describe such excitonic effects, within an effective one-particle picture, contrary to common belief. For being able to describe the optical electron-hole excitations one invariably assumes that an effective two-body approach is required, and therefore, in principle, TDDFT should not be able to resolve the excitonic features in the calculated optical absorption spectra.

In the last chapter, the longitudinal polarizability of several infinite conjugated polymers is investigated using the periodicity of these systems. The results as calculated by our TDDFT implementation overestimated the polarizability for all the polymers considered, when compared to the results as found by more traditional calculation methods. The overestimation is caused by an incorrect description of the macroscopic exchange-correlation electric field contribution in the local density approximation for the exchange-correlation functional. An estimate for the value of this counteracting macroscopic exchange-correlation contribution is given for all the considered polymers. This contribution is calculated in the form of a polarization functional, as was introduced in Chapter 7. It remains to be demonstrated whether such a polarization functional exists, which is indeed able to reproduce correctly these values.

